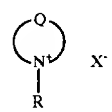
efficiency can be improved by using the dyes having a high light-absorbability as a mixture.

As explained above in detail, the electrolyte composition of the present invention is excellent in the durability and charge-transporting capability. The photoelectric conversion device comprising the electrolyte composition exhibits the excellent photoelectric conversion properties and less deterioration of the properties during the long-term use or storage. The photo-electrochemical cell composed of the device is remarkably useful as a solar cell.

What is claimed is:

1. An electrolyte composition comprising a compound represented by the following general formula (1):

(1)



wherein R represents a substituent containing a $-(CR_1R_2-CR_3R_4-O)_n-$ bond, in which R_1 to R_4 are independently a hydrogen atom or an alkyl group, n being an integer of 2 to 20, and said $-(CR_1R_2-CR_3R_4-O)_n-$ bond has a straight chain structure and directly bonds to N^+; Q represents an atomic group forming an aromatic cation having a 5- or 6-membered ring structure with a nitrogen atom, and optionally has a substituent; and X^- represents an anion.

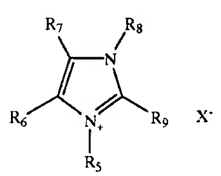
2. The electrolyte composition according to claim 1, wherein said Q has a substituent containing a $-(CR_1R_2-CR_3R_4-O)_n-$ bond, in which R_1 to R_4 are independently a hydrogen atom or an alkyl group, n being an integer of 2 to 20.

3. The electrolyte composition according to claim 1, wherein said Q is composed of atoms selected from the group consisting of carbon, hydrogen, nitrogen, oxygen and sulfur atoms.

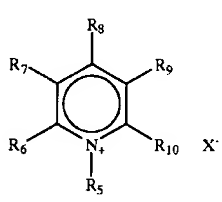
4. The electrolyte composition according to claim 1, wherein said 5- or 6-membered ring formed by Q is an imidazole ring or a pyridine ring.

5. The electrolyte composition according to claim 1, wherein said compound represented by the general formula (1) is further represented by the following general formula (2) or (3):

(2)



(3)



wherein R_5 represents a substituent containing a $-(CR_1R_2-CR_3R_4-O)_n-$ bond, in which R_1 to R_4 are independently a hydrogen atom or an alkyl group, n being an integer of 2 to 20, and said $-(CR_1R_2-CR_3R_4-O)_n-$ bond has a straight-chain structure and directly bonds to N^+; R_6 to R_{10} independently represent a hydrogen atom or a substituent; X^- represents an anion; and two or more of said R_6 to R_{10} optionally bond together to form a ring.

6. The electrolyte composition according to claim 1, wherein said n is an integer of 2 to 6.

7. The electrolyte composition according to claim 1, wherein the total number of $-CR_1R_2-CR_3R_4-O-$ bonds, in which R_1 to R_4 are independently a hydrogen atom or an alkyl group, in said compound represented by the general formula (1) is 4 to 6.

8. The electrolyte composition according to claim 1, wherein said X^- is I^-, $N^-(CF_3SO_2)_2$, BF_4^-, R_a-COO^- in which R_a is a hydrogen atom, an alkyl group, a perfluoroalkyl group or an aryl group, $R_bSO_3^-$ in which R_b is an alkyl group, a perfluoroalkyl group or an aryl group, or SCN^-.

9. The electrolyte composition according to claim 8, wherein said X^- is I^-.

10. The electrolyte composition according to claim 1 further comprising an iodine salt in addition to said compound represented by the general formula (1).

11. The electrolyte composition according to claim 10, wherein a cation of said iodine salt is a nitrogen-containing aromatic cation having a 5- or 6-membered ring structure.

12. The electrolyte composition according to claim 9 further comprising a salt that contains an anion selected from the group consisting of $N^-(CF_3SO_2)_2$, BF_4^-, R_a-COO^- in which R_a is a hydrogen atom, an alkyl group, a perfluoroalkyl group or an aryl group, $R_b-SO_3^-$ in which R_b is an alkyl group, a perfluoroalkyl group or an aryl group, and SCN^-.

13. The electrolyte composition according to claim 12, wherein a cation of said salt is a nitrogen-containing aromatic cation having a 5- or 6-membered ring structure.

14. The electrolyte composition according to claim 1 further comprising iodine.

15. The electrolyte composition according to claim 1, wherein a solvent-content is 10 weight % or less based on the total weight of the composition.

16. A photoelectric conversion device having an electrically conductive layer, a photosensitive layer, a charge transfer layer and a counter electrode, wherein said charge transfer layer comprises said electrolyte composition according to claim 1.

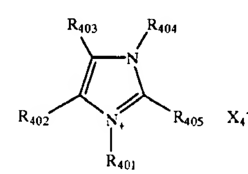
17. The photoelectric conversion device according to claim 16, wherein said photosensitive layer comprises semiconductor fine particles sensitized by a dye.

18. The photoelectric conversion device according to claim 17, wherein said semiconductor fine particles are composed of a metal chalcogenide.

19. A photo-electrochemical cell composed of said photoelectric conversion device according to claim 16.

20. An imidazolium compound represented by the following general formula (4):

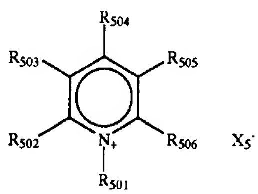
(4)



wherein R_{401} represents a substituent; R_{402} to R_{405} independently represent a hydrogen atom or a substituent; R_{401} and at least one of R_{402} to R_{405} independently contain a

$-(CR_1R_2-CR_3R_4-O)_n-$ bond, in which R_1 to R_4 are independently a hydrogen atom or an alkyl group, n being an integer of 2 to 20, and said $-(CR_1R_2-CR_3R_4-O)_n-$ bond contained in R_{401} has a straight-chain structure and directly bonds to N^+; X_4^- represents I^-, Cl^-, Br^-, $N^-(CF_3SO_2)_2$, $N^-(CF_3CF_2SO_2)_2$, $C^-(CF_3SO_2)_3$, BF_4^-, BPh_4^-, PF_6^-, ClO_4^-, R_a-COO^- in which R_a is a hydrogen atom, an alkyl group, a perfluoroalkyl group or an aryl group, $R_b-SO_3^-$ in which R_b is an alkyl group, a perfluoroalkyl group or an aryl group, or SCN^-; and two or more of R_{402} to R_{405} are optionally bonded together to form a ring.

21. A pyridinium compound represented by the following general formula (5):



(5)

wherein R_{501} represents a substituent; R_{502} to R_{506} independently represent a hydrogen atom or a substituent; R_{501} and at least one of R_{502} to R_{506} independently contain a $-(CR_1R_2-CR_3R_4-O)_n-$ bond, in which R_1 to R_4 are independently a hydrogen atom or an alkyl group, n being an integer of 2 to 20, and said $-(CR_1R_2-CR_3R_4-O)_n-$ bond contained in R_{501} has a straight-chain structure and directly bonds to N^+; X_5^- represents I^-, Cl^-, Br^-, $N^-(CF_3SO_2)_2$, $N^-(CF_3CF_2SO_2)_2$, $C^-(CF_3SO_2)_3$, BF_4^-, BPh_4^-, PF_6^-, ClO_4^-, R_a-COO^- in which R_a is a hydrogen atom, an alkyl group, a perfluoroalkyl group or an aryl group, $R_b-SO_3^-$ in which R_b is an alkyl group, a perfluoroalkyl group or an aryl group, or SCN^-; and two or more of R_{502} to R_{506} are optionally bonded together to form a ring.

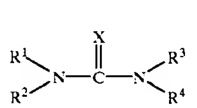
* * * * *

toelectric conversion devices was measured with respect to the photoelectric conversion efficiency in the same manner as Example 3. As a result, the photoelectric conversion devices of the present invention, in which the semiconductor fine particle was treated with the compounds (I) and (II), exhibited more excellent photoelectric conversion efficiency than those of the comparative photoelectric conversion devices.

[0236] As described in detail above, a photoelectric conversion device excellent in photoelectric conversion efficiency can be produced by a method of the present invention comprising the step of treating a semiconductor fine particle with a compound (I). The photoelectric conversion efficiency is further improved when the semiconductor fine particle is treated with each of the compound (I) and the compound (II).

What is claimed is:

1. A method for producing a photoelectric conversion device comprising a conductive support and a photosensitive layer containing a semiconductor fine particle on which a dye is adsorbed, wherein said semiconductor fine particle is treated with a compound represented by the following general formula (I):



(I)

wherein X represents an oxygen atom, a sulfur atom, a selenium atom or NY, in which Y represents a hydrogen atom, an aliphatic hydrocarbon group, a hydroxyl group or an alkoxy group; R^1, R^2, R^3 and R^4 independently represent a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, a heterocyclic group, $—N(R^5(R^6)$, $—C(=O)R^7$, $—C(=S)R^8$, $—SO_2R^9$ or $—OR^{10}$; R^5 and R^6 independently have the same meaning as said R^1, R^2, R^3 and R^4; R^7, R^8 and R^9 independently represent a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, a heterocyclic group, $—N(R^5)(R^6)$, $—OR^{10}$ or $—SR^{11}$; and R^{10} and R^{11} independently represent a hydrogen atom or an aliphatic hydrocarbon group.

2. The method for producing a photoelectric conversion device according to claim 1, wherein said semiconductor fine particle is treated with a solution comprising said compound represented by the general formula (I).

3. The method for producing a photoelectric conversion device according to claim 1, wherein said semiconductor fine particle is treated with said compound represented by the general formula (I) after said dye is adsorbed on said semiconductor fine particle.

4. The method for producing a photoelectric conversion device according to claim 3, wherein said semiconductor fine particle is treated with a compound having a basic group while said semiconductor fine particle is treated with said compound represented by the general formula (I).

5. The method for producing a photoelectric conversion device according to claim 4, wherein said compound having a basic group is pyridine or a derivative thereof.

6. The method for producing a photoelectric conversion device according to claim 1, wherein said semiconductor fine particle is treated with said compound represented by the general formula (I) while said dye is adsorbed on said semiconductor fine particle.

7. The method for producing a photoelectric conversion device according to claim 1, wherein said semiconductor fine particle is treated with said compound represented by the general formula a) and a compound represented by the following general formula (II):

$$M_{p}.Z_{q} \qquad (II)$$

wherein M represents an alkaline metal ion, an alkaline earth metal ion, an ammonium ion, an imidazolium ion or a pyridinium ion; Z represents a halide ion, a carboxylate ion, a sulfonate ion, a phosphonate ion, a bis-sulfonylimide ion, a tris-sulfonylmethide ion, a sulfate ion, a thiocyanate ion, a cyanate ion, a perchlorate ion, a tetrafluoroborate ion or a hexafluorophosphate ion; and p and q independently represent an integer of 1 or more.

8. The method for producing a photoelectric conversion device according to claim 7, wherein said semiconductor fine particle is treated with a solution comprising said compound represented by the general formula (I) and a solution comprising said compound represented by the general formula (II), or with a solution comprising said compound represented by the general formula (I) and said compound represented by the general formula (II).

9. The method for producing a photoelectric conversion device according to claim 7, wherein said semiconductor fine particle is treated with said compound represented by the general formula (I) after said dye is adsorbed on said semiconductor fine particle, and said semiconductor fine particle is treated with a compound having a basic group while said semiconductor fine particle is treated with said compound represented by the general formula (I).

10. The method for producing a photoelectric conversion device according to claim 9, wherein said compound having a basic group is pyridine or a derivative thereof.

11. The method for producing a photoelectric conversion device according to claim 7, wherein said semiconductor fine particle is treated with said compound represented by the general formula (I) while said dye is adsorbed on said semiconductor fine particle, and said semiconductor fine particle is then treated with said compound represented by the general formula (II).

12. The method for producing a photoelectric conversion device according to claim 7, wherein said semiconductor fine particle is treated with said compound represented by the general formula (II) while said dye is adsorbed on said semiconductor fine particle, and said semiconductor fine particle is then treated with said compound represented by the general formula (I).

13. The method for producing a photoelectric conversion device according to claim 1, wherein said X is an oxygen atom.

14. The method for producing a photoelectric conversion device according to claim 1, wherein said compound represented by the general formula (I) has $—Si(R^{12})(R^{13})(R^{14})$, in which R^{12}, R^{13} and R^{14} independently represent a hydroxyl group, an alkoxy group, a halogen atom, an

isocyanate group or an aliphatic hydrocarbon group, at least one of R^{12}, R^{13} and R^{14} being an alkoxy group, a halogen atom or an isocyanate group.

15. The method for producing a photoelectric conversion device according to claim 1, wherein said dye is a ruthenium complex dye.

16. A photoelectric conversion device obtained by the method recited in claim 1.

17. A photoelectric cell comprising the photoelectric conversion device recited in claim **16**.

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* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the high sensitivity photo detector which has the function to change change of the quantity of light into an electrical signal by the quick speed of response.
[0002]
[Description of the Prior Art] Conventionally, the photo detector which shows differential responsibility is attained by the electrochemical cell which already consists of composition of a transparent electrode / bacteriorhodopsin thin film / electrolyte / counter electrode (references, such as JP,3-205520,A, Miyasaka, Koyama, and and Itoh Science 255 342 1992).
[0003]
[Problem(s) to be Solved by the Invention] Although such a photo detector was known as first example which shows a differentiated type response on material level and it had many merits, the greatest fault was that sensitivity is very low. Moreover, we were anxious also about the stability by the relation which uses protein as a basic material.
[0004] Drawing 3 is drawing showing the response pattern of this conventional photo detector (it mentions later by the relation with the effect of this invention). this invention removes the above-mentioned trouble, its speed of response is quick, and it aims at offering the high sensitivity photo detector which was moreover excellent in stability.
[0005]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is equipped with a transparent electrode, an ion conductivity electrolyte, and a semiconductor electrode, and it is made to output a time differential type photoelectrical response to quantity of light change in [1] high-sensitivity photo detector.
[0006] [2] In the high sensitivity photo detector of the above-mentioned [1] publication, the aforementioned semiconductor electrode is silicon.
[3] In the high sensitivity photo detector of the above-mentioned [2] publication, the aforementioned silicon is n form silicon.
[4] In the high sensitivity photo detector of the above-mentioned [2] publication, the aforementioned silicon is p form silicon.
[0007] [5] In the high sensitivity photo detector of the above-mentioned [1] publication, the aforementioned ion conductivity electrolyte is a solid electrolyte.
[6] In the high sensitivity photo detector of the above-mentioned [1] publication, the speed of response of a standup is the high speed for 20 or less microseconds.
[0008]
[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained in detail, referring to a drawing. Drawing 1 is the block diagram of a high sensitivity photo detector showing the example of this invention. As shown in this drawing, the high sensitivity photo detector has composition which sandwiches the ion conductivity electrolyte 2 between a transparent electrode 1 and the silicon electrode (silicon substrate) 3 as an operation pole.

[0009] While the resistance 4 (a speed of response becomes quick as resistance becomes small) for adjustment of a speed of response is connected between the external terminals of this high sensitivity photo detector, the output line of a silicon substrate 3 is carried out ground 5. The oscilloscope 8 is connected between the output terminal 6 and 7. When the light was irradiated from the transparent-electrode 1 side at the high sensitivity photo detector of such composition, after the early standup of a photocurrent was observed by the external circuit, it returned to the zero level as it is, and optical OFF described the opposite direction for the photocurrent, and it returned to the original level. It has so-called time differential type responsibility.
[0010] An anode side will be touched with the photocurrent at the time of optical ON if n form is used for the silicon electrode 3 at this time. If it puts in another way, an electron will move to the silicon electrode 3 side from the ion conductivity electrolyte 2, and an electron will move to the ion conductivity electrolyte 2 side from the silicon electrode 3 side at the time of optical OFF. A pattern with the silicon electrode 3 reverse in p form is obtained. That is, a cathode side is touched with the photocurrent at the time of optical ON. If it puts in another way, an electron will move to the ion conductivity electrolyte 2 side from the silicon electrode 3 side, and an electron will move to the silicon electrode 3 side from the ion conductivity electrolyte 2 side at the time of optical OFF.
[0011] [Example] The electrochemical cell of 2 electrode system as shows 0.1 mol (NaCl etc. is sufficient) of KCl(s) to drawing 1 as SnO2 and an ion conductivity electrolyte 2 using n form silicon substrate which is an operation pole as a transparent electrode 1 was constituted. The thickness of the ion conductivity electrolyte 2 was set as 1mm. 150W xenon light was exposed for 0.25 seconds through IR (infrared radiation) cut-off filter and the yellow filter (Hoya Y48) in this cell.
[0012] Drawing 2 is drawing showing the response pattern of the high sensitivity photo detector which used n form silicon substrate which shows the example of this invention. The response of the high sensitivity photo detector of this invention is understood that improvement of the response sensitivity is carried out thousands times (memory V pair mV of a vertical axis) as compared with the response of the conventional photo detector shown in drawing 3 so that clearly from this drawing. It is completely satisfactory at the relation from which all stability also consists of inorganic material.
[0013] Thus, according to this invention, compared with the conventional cell, at least 1 or more figures has improved by 3 figures and the speed of response by sensitivity by using the silicon electrode 3 as an operation pole. Furthermore, explanation of an electrode uses preferably various kinds of noble metals (Au, Pt, etc.) or conductive metallic oxides (SnO2, In 2O2, RuO2, etc.) as a transparent electrode. A thing desirable in respect of light-transmission nature especially is the thin film (1000A or less in thickness) of Au or Pt or SnO2, and In 2O2. And it is the thin film of these complex (ITO). Especially the thing that is preferably used also in these in respect of the S/N ratio of the current in the chemical stability of an electrode material and an optical response in addition to the goodness of light-transmission nature is SnO2. And it is ITO.
[0014] SnO2 It reaches and the conductivity of ITO is 102 as conductivity. omega-1 cm to more than [1] is desirable, and it is 103. omega-1 cm to especially more than [1] is desirable. These conductive electrode materials are supported as a thin film by the vacuum deposition method, the sputtering method, etc. on transparent base materials, such as glass and a resin, and its 500-6000A is [the thin film] especially preferably desirable 100-10000A.
[0015] Next, when an electrolyte is described, the solid electrolyte which the electrolyte used as a medium of ion conductivity [this invention] turns into from electrolysis solution, inorganic material, or a macromolecule organic material is contained. the solution in which electrolysis solution contains a supporting electrolyte -- it is -- as a supporting electrolyte -- KCl, NaCl, K2 SO4, KNO2, LiCl, and NaClO4 etc. -- it is used
[0016] The concentration of a supporting electrolyte is usually 0.01 mols/l. - two mols/l., and is 0.05 mols/l. - one mol/l. preferably. What the polyelectrolyte through a macromolecule organic material is preferably used as a solid electrolyte, for example, contains moisture through gelatin, an agar, a polyacrylamide, polyvinyl alcohol, a general-purpose cation and anion exchange resins, or such mixture if as required for this as an ion carrier as a supporting electrolyte is used.
[0017] moreover -- as a solid electrolyte -- H+-WO3 A system and Na+-beta-aluminum 2O3 A system, a K+-ZnO system, PbCl2 /2 etc. -- the polyelectrolyte which makes it come as an ion carrier in the medium

of high molecular compounds, such as gelatin besides a deoxidization object, an agar, polyvinyl alcohol, a general-purpose cation exchange resin, and an anion exchange resin, to contain a salt can also be used [KCl and SnCl2]

[0018] In addition, in the above-mentioned example, although the example of 2 electrode system was given, if required, the reference electrode may be included as 3rd electrode element, and a reference electrode will be inserted into an ion conductivity electrolyte in this case. Under the present circumstances, voltage may be impressed from the exterior between the reference pole, the operation pole, or the transparent electrode. In the cell of 3 pole composition, a potentiostat (potentiostat) is mentioned as one of the things useful as a setup of the external circuit containing the metering device of current.

[0019] When using the 3rd electrode, although a desirable thing is silver/silver silver chloride electrode, a mercury chloride electrode, or a saturated calomel electrode, for minute-izing of the configuration of an element, silver/silver silver chloride electrode is used preferably. The gestalt of a thin film or a substrate is sufficient as the configuration of these counter electrodes and a reference electrode, and the configuration of a minute probe is sufficient as it. This response profile has been reproduced without decreasing also to thousands of exposure. carrying out the spectrum of the light source using a band pass filter -- the spectrum of a response -- as a result of measuring a spectrum, the strong response was obtained throughout the about 400 to 700nm light

[0020] Moreover, the speed of response of a standup is as high-speed as 20 or less microseconds. Thus, the high sensitivity photo detector of this invention has the function to change change of light into an electrical signal quickly, and can constitute a photosensor, an optical switch, an artificial retina, etc. as a useful element in engineering. In addition, in the external circuit of a high sensitivity photo detector, it can be carried out suitably if needed that it is made to perform wave processing of adding and amplifying amplifier etc.

[0021] Moreover, this invention is not limited to the above-mentioned example, and based on the meaning of this invention, various deformation is possible for it and it does not eliminate these from the range of this invention.

[0022]

[Effect of the Invention] As mentioned above, according to this invention, the following effects can be done so as explained in detail.

(A) A speed of response is quick and can offer the high sensitivity photo detector which was moreover excellent in stability.

[0023] (B) Change of light is quickly convertible for an electrical signal. In this case, the silicon substrate as an operation pole can be changed for the direction of the photocurrent outputted by selection of n form or p form.

(C) A photosensor, an optical switch, an artificial retina, etc. can be constituted as a useful element in engineering.

[Translation done.]